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Status Assessment of Toxic Chemicals

Acrylonitrile

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16. ABSTRACT

This report identifies the services and effects of environmental contaminators by acrylonitrile, as well as the health hazards resulting from such contamination. The present manufacturing processes, uses, control technologies, and regulatory actions are described, and areas requiring further study are indicated.

17. KEY WORDS AND DOCUMENT ANALYSIS

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STATUS ASSESSMENT OF TOXIC CHEMICALS: ACRYLONITRILE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of benzidine. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
Director
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ABSTRACT

An overview is given describing acrylonitrile sources, environmental contamination, health effects, control technology and regulatory action. Areas where information is needed include the amount of acrylonitrile emissions caused by its use as a raw material and the environmental levels of acrylonitrile resulting from its production and consumption.

Approximately 860,000 metric tons of acrylonitrile are produced and consumed in the U.S. annually. Of this amount, 42% is used in making acrylic fibers; 19% is used for the production of ABS and SAN resins and 4% for nitrile elastomer production. The remaining acrylonitrile produced is either exported or used in manufacturing miscellaneous products.

Acrylonitrile emissions resulting from its production and transportation have been estimated at 696 metric tons/yr. An additional 37 metric tons/yr are discharged to waterways during transport. Information is needed concerning the release of acrylonitrile from products composed of acrylonitrile copolymers.

Estimates indicate that no persons are exposed to concentrations of nitriles above 0.07 ppm from a representative acrylonitrile production facility. However, possible health effects from low-level chronic exposure of acrylonitrile to a population have not been documented.

Technology is available to control acrylonitrile emissions from various sources. Incineration is used to control emissions from process vent streams during acrylonitrile production. Methods used to control emissions of acrylonitrile during storage and transfer include vapor recovery systems, submerged filling and floating roof tanks with double seals.

Government regulations involving acrylonitrile-based products have been proposed or initiated, soft-drink bottles made from acrylonitrile copolymers have been banned from the consumer market by the FDA. A Threshold Limit Value of 45 mg/m^3 has been established as a workplace exposure standard. It is expected that this standard will be revised downward. Present use of acrylonitrile as a grain fumigant is being considered for cancellation by EPA.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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SYMBOLS AND ABBREVIATIONS

ABS -- acrylonitrile-butadiene-styrene resins
SAN -- styrene acrylonitrile resins
TLV® -- Threshold Limit Value

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Pound-mass	2.205×10^{3}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Joule (J)	Calorie (kg)	2.386×10^{-4}
Joule (J)	Newton-meter	1.000

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\epsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

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SECTION 1

INTRODUCTION

Acrylonitrile, an important synthetic organic chemical, is used in a wide variety of products with broad consumer distribution. It is a primary feedstock (or chemical intermediate) in the manufacture of acrylic fibers, nitrile rubber and plastic resins. There is, however, concern of adverse health effects to the general population from acrylonitrile exposure due to its toxicity.

There is a need to define the various sources from which acrylonitrile may enter the environment, to establish the consequent health and environmental effects, and to examine possible control strategies and present regulatory actions. This report provides a brief overview describing these items with emphasis on acrylonitrile sources and the resulting environmental significance.

SECTION 2

SUMMARY

Acrylonitrile is a commercially significant synthetic organic chemical with 862,000 metric tons[a] produced nationally in 1976. It is manufactured in the United States solely by the SOHIO process.

Physiological studies indicated that acrylonitrile in air is toxic to animals in the range of 0.1 g/m^3 to 1.0 g/m^3. It is considered toxic to man having an established Threshold Limit Value (TLV®) of 45 mg/m^3.

For a representative acrylonitrile plant, acrylonitrile emissions total 0.807 g/kg of acrylonitrile produced. Acrylonitrile emissions due to its use as a raw material in manufacturing other products or product use have not been documented. Acrylonitrile has been qualitatively identified in effluents from chemical acrylamide fiber and latex plants.

Figure 1 indicates potential sources of acrylonitrile pollution. Hydrocarbon emissions from process vents during acrylonitrile production are controlled by incineration and flaring. Emissions from storage of acrylonitrile can be controlled by floating roof tanks, internal floating covers, variable vapor space tanks, flaring, and conservation vents. Plant wastewaters are currently deep-well injected.

Possible emergency controls over worker exposure to acrylonitrile may be the outcome of recent epidemiological studies that show an increase in the cancer death-rate for workers exposed to acrylonitrile. The Food and Drug Administration (FDA) has regulated the acrylonitrile contents of nitrile rubber that comes into contact with food at 11 ppm (parts per million). The FDA has also withdrawn a permit for Monsanto to produce beverage containers from nitrile barrier resins.

Table 1 briefly describes acrylonitrile emission sources, their magnitude and control. Based on the information presented in this report, the following items need to be considered in future studies:

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[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages of this report.

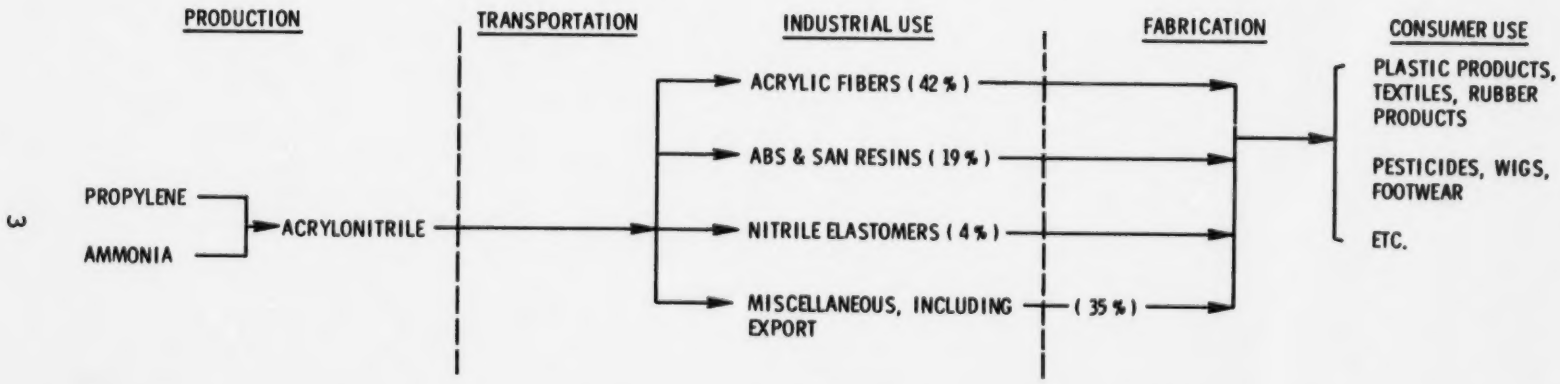

Figure 1. Potential sources of acrylonitrile pollution.

- Emission rates of acrylonitrile from industrial processes using it as a raw material.
- Rates of release of acrylonitrile from acrylonitrile-based products.
- Environmental levels of acrylonitrile.
- Chronic effects of low-level exposure to acrylonitrile.
- Atmospheric chemistry of acrylonitrile.

TABLE 1. ACRYLONITRILE SOURCES, THEIR MAGNITUDE AND CONTROL

Emission source	Extent of problem		Control method	Regulatory agency or action
	Emission quantity	Population exposed		
Production:				
Process vent streams	696 metric tons/yr (emitted to air from production and transportation).	EPA studies show no population at risk from levels in representative production facility.	Combustion or incineration devices.	OSHA has set threshold limit of 45 mg/m^3 as workplace exposure standard; to be revised downward.
Leaks, spills, and fugitive emissions			Improved maintenance and good housekeeping practices.	
Storage and transfer operations			Methods used for petroleum product storage and transfer including vapor recovery, submerged filling, and floating roof tanks with double seals.	Acrylonitrile is listed as a priority pollutant under the Federal Water Pollution Control Act.
Transportation:				
Spills, ballasting and other transit losses	37 metric tons/yr (1970) emitted to ocean.	No data available.	Vapor recovery during loading and unloading operations, proper containment and cleanup procedures for spills.	Unknown.
Industrial use:				
Acrylic fibers (42%)[a]	Literature indicates that the total quantity of emissions is not large.	Industrial workers are exposed to unknown levels of acrylonitrile in combination with other volatile organic substances.	Vapor recovery and combustion; improved monomer recovery and recycle; improved hood, vent, and exhaust systems.	Acrylonitrile as grain fumigant being considered for cancellation by FIFRA (EPA).
ABS and SAN resins (19%)[a]				
Nitrile elastomers (5%)[a]				
Miscellaneous, including export (35%)[a]	Unknown.	Unknown.	Unknown.	Unknown.
Emissions produced from polymerization, fiber spinning and resin and elastomer fabrication formulation				
Consumer use of end products	Unknown low levels.	Unknown, possible widespread chronic exposure to low level of acrylonitrile.	Better monomer recovery during industrial use; product substitution.	Ban on bottles from acrylonitrile copolymers (FDA).
				Present monomer limit on copolymer in contact with food set at 11 ppm.
				Propose to lower acrylonitrile migration limit (from copolymer) from 0.3 ppm to 0.05 ppm.

[a] Numbers in parentheses indicate consumption in 1976.

SECTION 3

SOURCE DESCRIPTION

PHYSICAL AND CHEMICAL PROPERTIES

Table 2 lists the physical and chemical properties of acrylonitrile (1).

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES OF ACRYLONITRILE (1)

Parameter	Property
Molecular weight	53.06
Boiling point	77.3°C
Freezing point	-83.5°C
Specific gravity	0.8060 at 20°C
Vapor density	1.83
Viscosity (liquid)	0.34×10^{-3} Pa-s at 24°C
Surface tension	27.3×10^{-7} N-m at 24°C
Flash point	0°C (open cup)
Latent heat of vaporization	33×10^{6} J/mole, vapor, 25°C
Refractive index	1.3888 at 25°C
Vapor pressure	6.7 kPa at 8.7°C 13 kPa at 23.6°C 33 kPa at 45.5°C 67 kPa at 64.7°C 101 kPa at 77.3°C
Dipole moment	3.3×10^{-18} esu-cm[a] (in carbon tetrachloride)
Solubility	5.35% at 20°C in water (solubility of water is 3.1% in acrylonitrile). Soluble in acetone, benzene, carbon tetrachloride, ether, ethyl acetate, ethylene cyanohydrin, methanol, petroleum ether, toluene, xylene, kerosene, and most other common organic solvents.

[a] Electrostatic unit-centimeter is nonmetric unit, unknown equivalent.

(1) Handbook of Chemistry and Physics, 55th Edition. R. C. Weast, ed., CRC Press, Cleveland, Ohio, 1974. I-151 pp.

PRODUCTION

Four companies manufacture acrylonitrile at six locations in the United States. Table 3 list manufacturers, plant locations and capacities. Most plants operate at or near capacity.

TABLE 3. ACRYLONITRILE PLANTS (2-4)

Company	Location	Capacity, metric tons/yr
American Cyanamid Co.	New Orleans, LA	91,000
Du Pont Co.	Beaumont, TX	160,000
Du Pont Co.	Memphis, TN	130,000
Monsanto Co.	Alvin, TX	200,000
Monsanto Co.	Texas City, TX	190,000
Vistron Corp.	Lima, OH	91,000
TOTALS		862,000

PROCESS DESCRIPTION

Acrylonitrile is manufactured in the United States exclusively from propylene and ammonia by the SOHIO process (2). The reaction may be represented by the following chemical equation:

$$2CH_2{=}CH{-}CH_3 + 2NH_3 + 3O_2 \rightarrow 2CH_2{=}CH{-}CN + 6H_2O$$

Propylene Ammonia Oxygen Acrylonitrile Water

Figure 2 is a flow sheet of a representative acrylonitrile plant (2, 5). The numbered streams are identified in Table 4.

(2) Hughes, T. W. and D. A. Horn. Source Assessment: Acrylonitrile Manufacture (Air Emissions), EPA-600/2-77-107j, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1977. 120 pp.

(3) Chemical Profile: Acrylonitrile. Chemical Marketing Reporter, 211(2):9, January 10, 1977.

(4) Statistical Abstract of the United States, 1974, 95th Edition. U.S. Department of Commerce, Bureau of the Census, Washington, D.C., 1974. pp. 445-461.

(5) Schwartz, W. A., F. B. Higgins, Jr., J. A. Lee, R. Newirth, and J. W. Pervier. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 2: Acrylonitrile Manufacture. EPA-450/3-73-006-b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 1975. 103 pp.

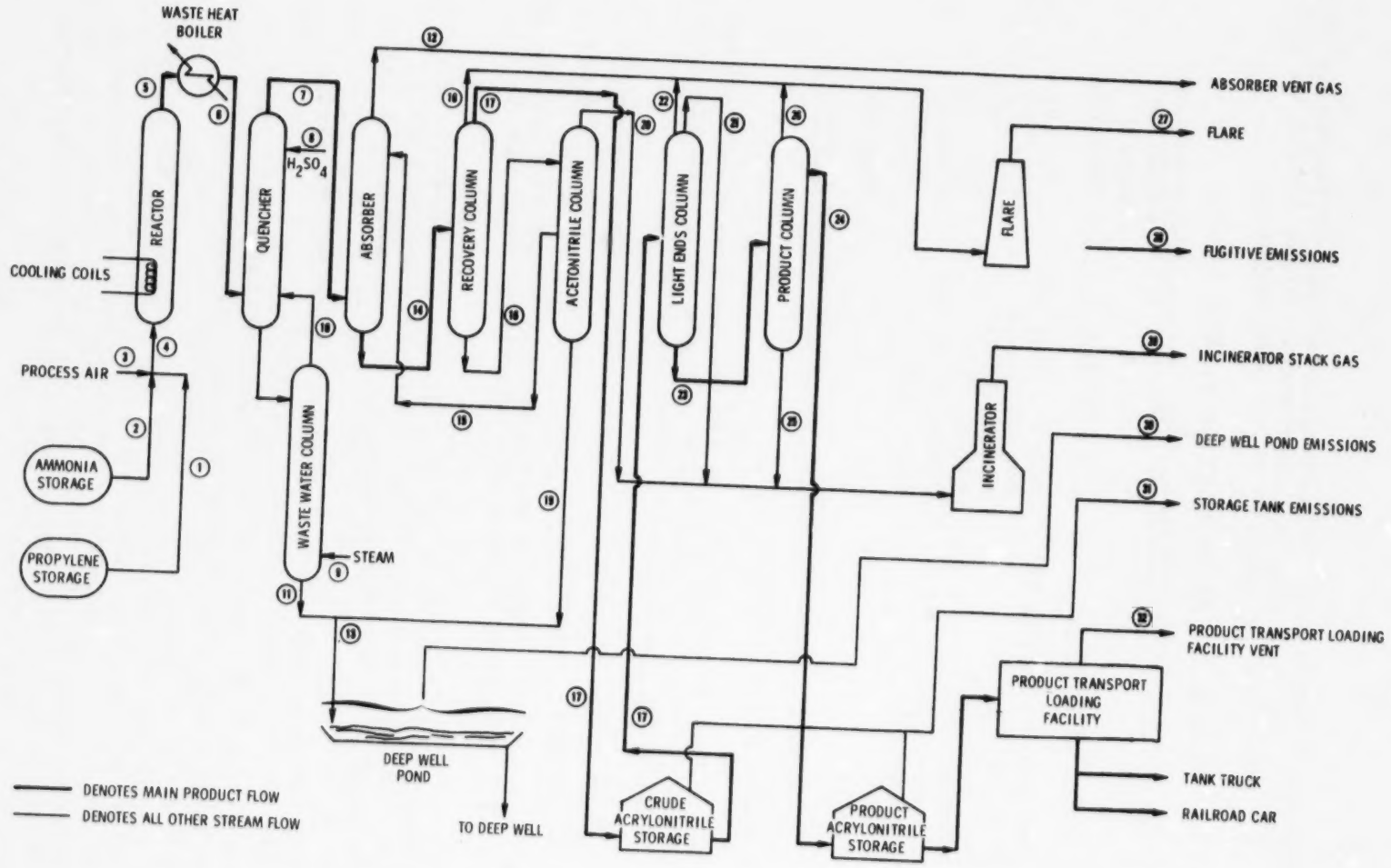

Figure 2. Flow diagram for a representative acrylonitrile plant (1, 2).

TABLE 4. STREAM CODES FOR FIGURE 2

Stream number	Description
1	Propylene feed
2	Ammonia feed
3	Process air
4	Reactor feed
5	Reactor product
6	Cooled reactor product
7	Quenched reactor product
8	Sulfuric acid
9	Stripping steam
10	Wastewater column volatiles
11	Wastewater column bottoms
12	Absorber vent gas
13	Acrylonitrile plant wastewater
14	Absorber bottoms
15	Water recycle
16	Crude acetonitrile
17	Crude acrylonitrile
18	Recovery column purge vent
19	Acetonitrile column bottoms
20	Acetonitrile
21	Hydrogen cyanide
22	Light ends column purge vent
23	Light ends column bottoms
24	Product acrylonitrile
25	Heavy ends
26	Product column purge vent
27	Flare
28	Fugitive emissions
29	Incinerator stack gas
30	Deep well pond emissions
31	Storage tank emissions
32	Product transport loading facility vent

Air, agricultural grade ammonia, and propylene (greater than 90% purity) in approximately stoichiometric proporations are introduced into a fluidized bed reactor at 125 kPa to 310 kPa and 400°C to 510°C (2, 5). Conversion of propylene is virtually complete, so that no recycle is required. The heat of reaction is used to generate process steam. The reactor effluent is sent to a water quench tower where unreacted ammonia is removed with sulfuric acid. The stream is then charged to an absorber to recover the reaction products. The resulting mixture of acetonitrile, acrylonitrile, and hydrogen cyanide is separated in a series of distillations. The final acrylonitrile product is 99+% pure.

By product acetonitrile and hydrogen cyanide are produced at 99+% purity for sales. Currently, only Vistron and DuPont market

acetonitrile products. In all plants, a portion (50%) of the hydrogen cyanide and most of the acetonitrile are incinerated.

Wastes generated during acrylonitrile production are a collection of gaseous, liquid and solid types. Emissions originate from the absorber vent (stream 12), incinerator (stream 29), flare (stream 29), deep well pond (stream 30), storage tanks (stream 31), product transport loading facility (stream 32), and fugitive emission points (stream 28) (2). Effluent streams are generated in the wastewater and acetonitrile columns (streams 11 and 19 in Figure 2). Catalyst fines from the reactor and organic polymers from the product columns (stream 25) make up the solid portion of acrylonitrile-produced wastes (2). The composition of air emissions and effluent streams are given in Section 4.

USES

Acrylonitrile is an important raw material in the production of acrylic fibers, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins, and nitrile elastomers. Table 5 shows acrylonitrile consumption by various industries in 1976 (6). Figure 3 is a product flow diagram for acrylonitrile (7).

TABLE 5. ACRYLONITRILE CONSUMPTION (1976) (6)

Use	Consumption, 10^3 metric tons/yr	Acrylonitrile consumed, %
Acrylic fibers	362	42
ABS and SAN resins	164	19
Nitrile elastomers	34	4
Exports	150	17.5
Miscellaneous	150	17.5
TOTAL	860	100

The acrylic fiber industry is an important consumer of acrylonitrile utilizing 42% of the acrylonitrile produced annually. Acrylic fibers contain at least 85% acrylonitrile by weight with modacrylic fibers containing 35% to 85% acrylonitrile. The amount of acrylonitrile consumed by this industry in 1976 was

(6) Chemical Origins and Markets, Fifth Edition. G. M. Lawler, ed., Chemical Information Services, Menlo Park, California, 1977. 118 pp.

(7) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 1. John Wiley & Sons, Inc., New York, New York, 1969. pp. 338-351.

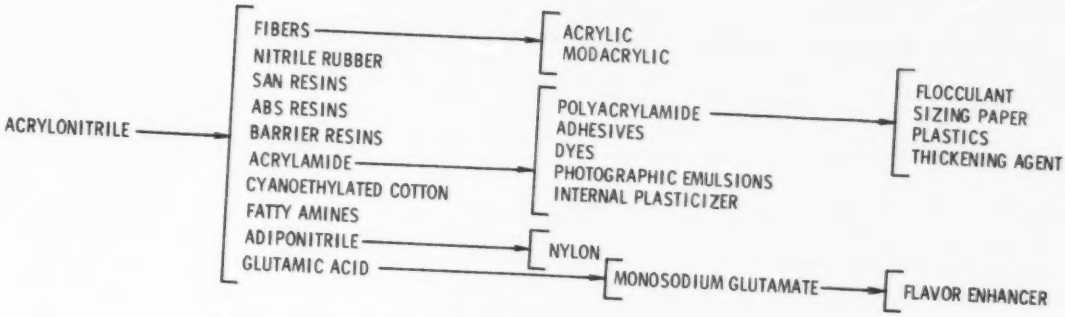

Figure 3. Acrylonitrile end uses (7).

362 x 10^3 metric tons. Table 6 lists manufacturers of acrylic fibers and fiber production.

TABLE 6. ACRYLONITRILE USED IN SYNTHETIC FIBER PRODUCTION (1976) (2)

Producer	Location	Fiber	Fiber production, 10^3 metric tons/yr
American Cyanamid	Milton, FL	A,M[a]	
Dow Badische Co.	Williamsburg, VA	A,M	57
E. I. DuPont de Nemours	Camden, SC	A,M	33
E. I. DuPont de Nemours	Wanesboro, VA	A	138
Tennessee Eastman Co.	Kingsport, TN	A,M	-[b]
Monsanto Corp.	Decatur, AL	A,M	18
			120

[a]A-acrylic, M-modacrylic. [b]Plant consumption not known.

Manufacturers of ABS plastic and nitrile rubber consume approximately 23% of the acrylonitrile produced annually. This amounted to 164 x 10^3 metric tons of acrylonitrile consumed in the production of ABS plastic for 1976. Production of nitrile rubber also consumed 34 x 10^3 metric tons of acrylonitrile.

Miscellaneous uses of acrylonitrile are as a chemical intermediate in the synthesis of antioxidants, pharmaceuticals, dyes, and surface active agents. In organic synthesis it is used 1) to introduce a cyanoethyl group, 2) as a feedstock for producing adiponitrile and acrylamide, 3) as a modifier for natural polymers, 4) as a cyanoethylating agent for cotton, and 5) in synthetic soil blocks (acrylonitrile polymerized in wood pulp). It is also used as a pesticide fumigant for stored grain, dried fruit, walnut, and tobacco. Acrylonitrile is a spot fumigant in flour mills and bakeries and is used as a gasoline additive (10, 11). The amount of acrylonitrile consumed in each of these various uses has not been found in the literature.

TABLE 7. PRODUCERS OF ABS RESINS (1976) (8)

Producer	Location	ABS production, 10^3 metric tons/yr
Borg-Warner Corp.	Ottawa, IL	91
Borg-Warner Corp.	Washington, VA	120
Rexene Polymers Co.	Joliet, IL	25
Dow Chemical, USA	Gales Feray, CT	29
Dow Chemical	Midland, MI	32
Dow Chemical	Pevely, MO	45
Dow Chemical	Torrance, CA	9
Foster Grant Co., Inc.	Leomister, MO	-[a]
B. F. Goodrich Co.	Louisville, KY	14
Carl Gorden Indust., Inc.	Workchester, MO	-[a]
Hammond Plastics Div.	Oxford, MA	-[a]
Monsanto Co.	Addyston, OH	145
Monsanto	Muscatine, IA	57
Union Carbide	Bound Brook, NJ	14
Uniroyal, Inc.	Baton Rouge, LA	91
Uniroyal	Scotts Bluff, LA	-[a]

[a]Blanks indicate data not available.

TABLE 8. PRODUCERS OF NITRILE RUBBER (1976) (9)

Producer	Location	Rubber type	Production, 10^3 metric tons/yr
Copolymer Rubber Co.	Baton Rouge, LA	NBR[a]	5
Firestone Tire & Rubber Co.	Akron, OH	NBR	5
B. F. Goodrich Co.	Akron, OH	NBR	14
B. F. Goodrich Co.	Louisville, KY	NBR	28
B. F. Goodrich Co.	Louisville, KY	NBR latex	-[c]
Goodyear Tire & Rubber Co.	Akron, OH	COX[b]	-[c]
Goodyear Tire & Rubber Co.	Akron, OH	COX	5
Standard Brands, Inc.	Beaumont, TX	NBR	11
Uniroyal, Inc.	Cheswold, DE	NBR	-[c]
	Baton Rouge, LA	NBR	14

[a]Buma N6 Nitrile.

[b]NBR modified with carboxylic groups.

[c]Production unknown.

(8) Chemical Profile: ABS Resins. Chemical Marketing Reporter, 205(16):9, April 29, 1974.

(9) Chemical Profile: Nitrile Rubber. Chemical Marketing Reporter, 210(17):9, October 25, 1976.

TRANSPORATION AND STORAGE

Fixed-roof storage tanks are used to store acrylonitrile product, crude acrylonitrile and acetonitrile prior to incineration (2).

Acrylonitrile is transported to the customer by one of four methods: railroad tank car, tanker truck, barge, or in 0.21-m^3 (55-gal) drums. Railroad tank car and tanker truck loading is accomplished by either top or bottom loading. Transportation of acrylonitrile to other industrial facilities is an important large-scale operation since it is a vital raw material in secondary industries such as acrylic fiber manufacturing.

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(10) Assessing Potential Ocean Pollutants. PB 240 917, U.S. Environmental Protection Agency, Washington, D.C., 1975. pp. 217-227.

(11) The Merck Index, Ninth Edition. M. Windholz, S. Budavari, L. Y. Stromtsos and M. N. Fertig, eds., Merck and Company, Inc., Rahway, New Jersey, 1976. pp. 127-128.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Acrylonitrile can be introduced into the environment from production, transportation, production of other products from acrylonitrile, or the use of products containing acrylonitrile.

Emissions from Acrylonitrile Production

Emissions from acrylonitrile production have been studied by EPA (2, 5). Table 9 contains emission factors for various emission points in production plants. Emission factors express the mass of emissions in grams per kilogram of acrylonitrile produced. The absorber vent gas consists of the reactor effluent after neutralization and recovery of nitriles and HCN.

TABLE 9. EMISSION FACTORS FOR ACRYLONITRILE DURING PRODUCTION (2)
(g/kg)

Absorber vent[a]	Incinerator stack	Flare	Fugitive emissions	Product transport and loading	Storage (all tanks)	Total
0.039 ± 41%	0.0015	0.039	0.00042 ± 20%	0.0065 ± 20%	0.722	0.807

[a]Emissions for process employing catalyst 41.

The byproduct streams which are usually incinerated are acetonitrile and hydrogen cyanide. Polymers, heavy ends, and wastewater are usually disposed of by deep well injection. During deep well injection pump failure (about once a year), these wastes are also incinerated. A flare is used to dispose of various hydrocarbon plant streams. Feed streams to the flare may be product fractionation vents, relief valves in propylene storage tanks and preheaters, and streams resulting from plant shutdown for equipment purging.

Fugitive emissions result from valves, flanges, pumps, compressors, and leaks in equipment. Product transport and loading emissions result from product transfer into containers, transport, and unloading of product at its destination. Storage loss emissions result from fixed roof tanks which are vented directly to the atmosphere.

Applying the total emission factor of 0.807 g/kg product to the capacity data presented in a previous section, results in an estimate of 612 metric tons/yr of acrylonitrile emitted to the air from production and transportation.

Unknown quantities of acrylonitrile have been found in plant wastewater from acrylonitrile production (2). It has been estimated that acrylonitrile discharged to the ocean from transport and handling amounted to 37 metric tons in 1970 (10).

Contamination from Industrial Applications of Acrylonitrile

Approximately 65% of acrylonitrile production is used in the U.S. to manufacture polymer materials including fibers, resins, and elastomers. Polymer production processes result in emissions of monomers and other chemicals. Emissions may occur from the reactor vents, runaway reactions in which a batch is dumped, product recovery, and extrusion. It has been estimated that only a small amount of acrylonitrile is lost in acrylic fiber manufacture (10). Twelve percent of acrylonitrile production is used in nine miscellaneous applications. The mass of emissions from these uses is unknown. Its use as a pesticide on agricultural products involves the potential hazard of its being ingested by man or entering the food chain.

Acrylonitrile Contamination from Product Use

Plastic and rubber products made from acrylonitrile polymers include clothing, carpeting, blankets, draperies, upholstery, wigs, imitation fur, sand bags, automobile parts, appliances, piping, tumblers, filaments, seals, gaskets, hoses, belts, adhesives, footwear, and brake linings. No studies have determined whether exposure of a population to chronic levels of acrylonitrile is occuring due to its release during product use. It has been suggested that acrylonitrile may be leached from fabrics in laundering processes. Polyacrylamide, containing trace amounts of acrylonitrile may also be a source of water contamination since it is used in water treatment operations.

Environmental Levels

Persons may be exposed to acrylonitrile as a result of production and storage, downstream chemical processing, transportation, and use of products containing acrylonitrile.

The use of a model in an EPA study of air emissions from acrylonitrile production predicted that no persons are exposed to concentrations of nitriles above 0.07 ppm from a representative acrylonitrile production facility (2).

While acrylonitrile is produced in only six locations, the number of downstream industrial processing facilities that use acrylonitrile is much larger. Acrylonitrile emission levels from these plants is not known. A study listing various organic compounds found in water show that acrylonitrile is present in wastewaters from acrylonitrile, acrylamide fiber, and latex plants (12).

Reactions and Pathways in the Environment

Reactions of acrylonitrile may involve the cyano group (CN), the activated double bond (C=C), or both groups. It reacts readily with olefins, alcohols, and aldehydes. The nitrile group can be converted to an amide or an organic acid in the presence of acids and bases, respectively. The double bond undergoes Diels-Alder and related reactions, halogenation and hydrogenation. Purified acrylonitrile will polymerize spontaneously. It polymerizes explosively in the presence of concentrated alkali.

Acrylonitrile can be removed from water by biological oxidation and organisms that are capable of adapting to nitrile oxidation are common in surface water (10, 13). Other studies show that nitrile oxidation results in the formation of organic acids and ammonia instead of HCN (14). The chemical reactivity and relative biodegradability of this molecule indicate that upon release to aquatic environments it would degrade and have a short residence time as acrylonitrile (10).

A description of the atmospheric chemistry of acrylonitrile is unknown. Half-life in the atmosphere and degradation products formed should be researched further. Because of its high reactivity, it is probable that acrylonitrile has a short residence time in atmospheric environments.

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(12) Shackelford, W. M. and L. H. Keith. Frequency of Organic Compounds Identified in Water. EPA-600/4-76-062, U.S. Environmental Protection Agency, Athens, Georgia, December 1976. 629 pp.

(13) Ludzaek, F. J., R. B. Schaffer, R. N. Bloomhuff and M. B. Ettinger. Biochemical Oxidation of Some Commercially Important Organic Cyanides, River Water Oxidations I. In: Proceedings of the Thirteenth Industrial Waste Conference, Purdue University, Lafayette, Indiana, 1958. pp. 292-312.

(14) Buzzell, J. C., Jr., R. H. F. Young and D. W. Ryckman. Behavior of Organic Chemicals in the Aquatic Environment, Behavior in Dilute Systems. Manufacturing Chemicals Association, Washington, D.C., 1968.

Secondary Emissions and Effluents

Emissions--
Table 10 contains emission factors for a number of pollutants resulting from acrylonitrile production. The table shows that a large amount of uncontrolled hydrocarbons is emitted to the atmosphere from the production process. Ninety-six percent (96%) of the hydrocarbons emitted are propylene and propane. The number of persons possibly exposed to concentrations above the Primary Ambient Air Quality standard for hydrocarbon emissions from a representative acrylonitrile plant is estimated at 13,300 (2).

Some quantities of hydrogen cyanide are also emitted. Although the byproduct stream is incinerated, small amounts of HCN can be emitted from the process. The same is true for acetonitrile.

Table 11 puts emissions from acrylonitrile into perspective with those from other organic chemical industries. Hydrocarbon emissions from acrylonitrile production are high when compared to emissions from other chemical manufacturing processes (5).

Wastewater--
Wastewater generated within an acrylonitrile plant contains ammonium sulfate, catalyst fines, organic polymers, and miscellaneous organic materials (2). This waste is sent to a deep-well pond where suspended solids are removed. The aqueous portion is deep-well injected. Table 12 shows the composition of acrylonitrile plant wastewater (2, 15).

HEALTH EFFECTS

To evaluate the potential health effects of acrylonitrile contamination in the environment, toxicity of acrylonitrile to animals and man is described.

Effects on Animals

Numerous animal studies are described in the literature. Table 13 contains some of the toxicity data generated in animal studies (16).

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(15) Train, R. E. Development Document for Interim Final Effluent Limitations and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA-400/1-75/045, U.S. Environmental Protection Agency, Washington, D.C., November 1975. 391 pp.

TABLE 10. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (UNCONTROLLED EMISSIONS) (2) (g/kg of acrylonitrile produced)

Material emitted	Emission point						
	Absorber vent	Incinerator stack	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Storage tanks
Criteria pollutants:							
Carbon monoxide	79.3 ± 6%	0.0040 ± 10%					
Hydrocarbons (as CH_4)[a]	57.1 ± 7%	0.0203 + 428% - 100%	0.268	13 ± 61%	0.00038 ± 20%	0.0055 ± 20%	0.661 ± 20%
Nitrogen oxides		0.542 + 107% - 100%	0.01				
Sulfur oxides		0.176 ± 59%					
Particulates							
Chemical substances:							
Methane	0.67 ± 6%	0.0023 ± 10%					
Ethane	1.93 ± 92%						
Ethylene	2.57 ± 81%						
Propane and propylene	55.0 ± 60%		0.022		0.000006 ± 20%		
Butene	0.400 ± 50%						
Benzene	0.146 ± 50%						
Toluene	0.065 ± 50%						
Acrylonitrile	0.039 ± 41%	<0.0015	0.039		0.00042 ± 20%	0.0065 ± 20%	0.802 ± 20%
Acetonitrile	0.625 ± 49%	<0.0015			0.000024 ± 20%		
Hydrogen cyanide	0.275 ± 22%	0.0343 + 428% - 100%	0.35				
Fumaronitrile				0.036			
Pyridine				5.2 ± 74%			
Propionaldehyde	0.0061 ± 50%						
Furan	0.467 ± 50%						
Ammonia					0.000006 ± 20%		
Allyl alcohol	0.024 ± 50%						

[a] Emission factors for total hydrocarbons do not equal the sum of emission factors for all organic materials except methane. To determine the hydrocarbon emission, the methane equivalent emission factors (based on carbon) for each nonmethane organic material are calculated and then summed. (Statement applies to all emission points except deep well pond where 7.8 g/kg of material [two species] were unidentifiable.)

Note: Blanks indicate no emissions present.

TABLE 11. EMISSIONS FROM ORGANIC CHEMICAL INDUSTRY (5)

Chemical	Estimated current air emissions, metric tons/yr[a]						
	Hydrocarbons[b]	Particulates[c]	Oxides of nitrogen	Sulfur oxides	Carbon monoxide	Total	Total weighted[d]
Acetaldehyde via ethylene	0.5	0	0	0	0	0.5	86
via ethanol	0	0	0	0	12	12	27
Acetic acid via methanol	0	0	0.004	0	0	0.004	1
via butane	18	0	0.02	0	6.3	24	3,215
via acetaldehyde	2.7	0	0	0	0.6	3.3	490
Acetic anhydride via acetic acid	1.4	0	0	0	2.5	3.9	253
Acrylonitrile[e]	83	0	2.5	0	88	174	15,000
Adipic acid	0	0.09	13	0	0.06	14	1,190
Adiponitrile via butadiene	5.1	2.1	23	0	0	30	3,200
via adipic acid	0	0.2	0.02	0	0	0.2	30
Carbon black	60	3.7	3.1	9.8	1,755	1,841	17,544
Carbon disulfide	0.07	0.1	0.05	2	0	2.3	120
Cyclohexanone	32	0	0	0	35	67	5,700
Dimethyl terephthalate (+TPA)	41	0.6	0.004	0.45	24	66	7,460
Ethylene	6.8	0.09	0.09	0.9	0.09	8	1,240
Ethylene dichloride via oxychlorination	43	0.2	0	0	9.9	53	7,650
via direct chlorination	13	0	0	0	0	13	2,300
Ethylene oxide	39	0	0.1	0.05	0	39	6,880
Formaldehyde via silver catalyst	11	0	0	0	49	59	1,955
via iron oxide catalyst	11.6	0	0	0	11	23	2,070
Glycerol via epichlorohydrin	7.2	0	0	0	0	7.2	1,280
Hydrogen cyanide (direct process)	0.2	0	0.2	0	0	0.4	56
Isocyanates	0.6	0.4	0	0.009	39	40	231
Maleic anhydride	15	0	0	0	118	133	2,950
Nylon 6	0	0.7	0	0	0	0.7	90
Nylon 6,6	0	2.5	0	0	0	2.5	330
Oxo process	2.4	0.004	0.03	0	8.8	11	440
Phenol	11	0	0	0	0	11	1,940
Phthalic anhydride via *o*-xylene	0.04	2.3	0.1	1.2	20	23	422
via naphthalene	0	0.9	0	0	20	21	160
High density polyethylene	36	1.0	0	0	0	37	6,400
Low density polyethylene	34	0.6	0	0	0	35	6,100
Polypropylene	17	0.05	0	0	0	17	2,950
Polystyrene	9.1	0.2	0	0.5	0	9.8	1,650
Polyvinyl chloride	28	5.4	0	0	0	33	5,700
Styrene	1.9	0.03	0.06	0	0	2	355
Styrene-butadiene rubber	4.2	0.7	0	0.4	0	5.4	870
Vinyl acetate via acetylene	2.4	0	0	0	0	2.4	425
via ethylene	0	0	TR[f]	0	0	TR	TR
Vinyl chloride	8	0.3	0	0	0	8.2	1,460
TOTALS	556	10	19	7	997	1,285	110,220[g]

[a] In most instances, numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.

[b] Excludes methane, includes hydrogen sulfide and all volatile organics.

[c] Includes nonvolatile organics and inorganics.

[d] Weighting factors used are: hydrocarbons - 80, particulates - 60, nitrogen oxides - 40, sulfur oxides - 20, and carbon monoxide - 1.

[e] Emissions based on what is now an obsolete catalyst.

[f] Trace amount.

[g] Totals are not equal across and down due to rounding.

TABLE 12. ACRYLONITRILE PLANT WASTEWATER (2, 15)

Material discharged	Concentration, mg/l	Effluent factor, g/kg
Raw wastewater	-[a]	4,470
Biological oxygen demand	8,620	38.7
Chemical oxygen demand	32,800	133
Total organic carbon	14,400	57.5
Total solids	36,700 to 57,800	163 to 182
Total suspended solids	184 to 630	0.915 to 1.78
Total dissolved solids	36,500 to 57,200	161 to 181
Oil and grease	135 to 168	0.475 to 0.657
Total nitrogen (as N_2)	4,040 to 22,000	16.9 to 62.1
Ammonia nitrogen (as N_2)	2,600 to 13,600	10.3 to 38.3
Nitrile nitrogen (as N_2)	197 to 270	0.755 to 0.97
Phosphate	0.152 to 6.15	0.0004 to 0.0298
Phenol	0.165 to 2.28	0.0007 to 0.0064
Sulfate	2,700 to 5,309	64.1 to 74.3
Zinc	0.052 to 2.1	0.00002 to 0.0092
Chloride	125 to 858	0.616 to 2.42
Iron	3.13 to 4.24	0.0088 to 0.0182
Copper	≤0.5	≤0.00024
Chromium	≤0.05	≤0.00014
Cadmium	≤0.05	≤0.00024

Other compounds which have been qualitatively identified include:

Acetaldehyde	Methacrylonitrile	Ammonium acetate
Acrolein	trans-Crotonitrile	Ammonium methacrylate
Hydrogen cyanide	cis-Crotonitrile	Ammonium acrylate
Acetic acid	Allyl cyanide	Succinonitrile
Fumaronitrile	Benzonitrile	Acetone
Acrylic acid	Nicotinonitrile	Acetaldehyde cyanohydrin
Acrylamide	Malononitrile	Acetone cyanohydrin
Acrylonitrile	Furonitrile	Acrolein cyanohydrin
Acetonitrile	Ticoline	Pyrazole
Maleonitrile	Lutidine compounds	Methyl pyrazine
Organic polymers	Benzene	Cyanopyrazine
Propionitrile	Toluene	Pyrazine
Ammonium formate		

[a]Not applicable.

TABLE 13. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF ACRYLONITRILE IN AIR FOR ANIMALS (16)

Animal	Concentration g/m^3	Concentration ppm	Response
Rat	1.38	636	Fatal after 4-hr exposure.
Rat	0.28	129	Slight transitory effect.
Rat	0.21	97	Slight transitory effects.
Rabbit	0.56	258	Fatal during or after exposure.
Rabbit	0.29	133	Marked transitory effects.
Rabbit	0.21	97	Slight transitory effects.
Cat	0.60	276	Markedly toxic.
Cat	0.33	152	Markedly toxic, sometimes fatal.
Guinea pig	1.25	576	Fatal during or after exposure.
Guinea pig	0.58	267	Slight transitory effect.
Dog	0.24	110	Fatal to three fourths of the dogs.
Dog	0.213	98	Convulsions and coma; no death.
Dog	0.12	55	Transitory paralysis; 1 dog died.
Dog	0.063	29	Very slight effects.

Effects on Humans

Acrylonitrile can be toxic when ingested, inhaled, or absorbed through the skin. It exhibits many of the effects of cyanide poisoning and is a severe skin and eye irritant (16).

The threshold limit value is 45 mg/m^3 (17). Vapor poisoning may result in nausea, vomiting, diarrhea, flushing, headache, salivation, sneezing, altered respiration, weakness, asphyxia, and loss of consciousness (16).

Chronic effects cited are inhibition of respiratory enzyme systems, irritation of eyes and nose, anemia, leucocytosis, and alteration of liver and kidney function (16).

Carcinogenicity is suspected, but studies are not yet complete. Preliminary indications are that workers exposed to acrylonitrile in acrylic fiber plants have a higher incidence of cancer of the lung and large intestine than the general population.

(16) Fassett, D. W. Cyanides and Nitriles. In: Industrial Hygiene and Toxicology, Chapter 44, F. A. Patty, ed. Interscience Publishers, New York, New York, 1962. pp. 2010-2011.

(17) TLV's® Threshold Limit Values for Chemical Substances and Physical Agents in the workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

SECTION 5

CONTROL TECHNOLOGY

Control methods, efficiencies, and economics are presented here for controlling emissions from production facilities. Technology for controls in production facilities is available for industrial use. This area of technology has been the subject of two EPA studies (2, 5).

Control methods for transportation losses are similar to those used in the petroleum industry and are defined in the literature (18). Control methods for downstream processing and use of products containing acrylonitrile need to be assessed.

CONTROL METHODS

Control of hydrocarbon emission from acrylonitrile production is described in the following subsection by noting applicable control technology for specific emission points in the process.

Absorber Vent Gas Control

The absorber vent gas emissions from acrylonitrile manufacture may be controlled with a combustion device such as a carbon monoxide boiler, thermal incinerator, catalytic incinerator, or flare (5). Presently, existing plants utilize only thermal or catalytic incineration for control of absorber vent gases (2).

Since hydrocarbon emissions result from incomplete conversion in the reactor, the acrylonitrile industry has thus far concentrated its efforts for reducing emissions on the development of more selective catalysts. Such catalysts would increase acrylonitrile production while lowering the amount of byproducts which are vented (2).

For new plants, the best control system may be a combination of thermal incineration with a waste heat boiler (5).

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(18) Control Techniques for Volatile Organic Emission from Stationary Sources, Draft Report. AP-68, by Radian Corporation, for U.S. Environmental Protection Agency, 1977.

Fractionating Column Vent Gas Control

Organic emissions in fractionation column vent gases may be controlled by combustion. Flaring is the generally accepted procedure in this case because the volume is small. Indications are that this control method is practiced widely in the industry (2).

Settling Pond Emission Control

Emissions from the settling pond are reduced by covering the surface with a high molecular weight oil (2). Emission factors for controlled and uncontrolled pond emissions are listed in Table 14.

TABLE 14. HYDROCARBON EMISSION FACTORS FOR ACRYLONITRILE DEEP WELL PONDS[a,b] (2)
(g/kg)

Component	Uncontrolled[c]	Controlled[d]	Percent reduction from use of control
Pyridine	5.2 ± 74%	0	∿100
Fumaronitrile	0.036	0	∿100
Methanol	0	0.2 ± 138%	0
Acetaldehyde	0	0.06 ± 423%	0
Ethanol	0	0.1 ± 315%	0
Butanes	0	0.06 ± 182%	0
Pentane	0	0.04 ± 172%	0
Hexanes	0	0.04 ± 145%	0
Benzene	0	0.1 ± 150%	0
Toluene	0	0.2 ± 222%	0
Others, unidentified	7.8	0	∿100
TOTAL HYDROCARBONS	13 ± 61%	0.62 ± 117%	95

[a] Deep well ponds may be used to treat wastewater generated at other chemical operations adjacent to acrylonitrile plants.

[b] Values shown represent mean values obtained at each plant, ± error as determined by the "Student's t" distribution (19).

[c] An uncontrolled deep well pond measures 60 m by 90 m and does not have any covering over the water surface.

[d] A controlled deep well pond measures 60 m by 90 m and is covered with a 0.1-m layer of lube oil having an average molecular weight of ∿500 g/g-mole.

(19) Student, A. (W. S. Gosset) The probable error of a mean. Biometrika, 6:1, 1908.

Control of Storage Tank Emissions

EPA reports on emissions from acrylonitrile production indicate that storage is one of the largest sources of emissions. This is also one of the easiest sources to control. There are two ways generally used to control emissions from storage of low volatility liquids. The first approach, applicable primarily to new construction, is to install storage tanks with lower loss rates than fixed cone roof tanks. Tanks with lower loss rates include floating roof tanks, internal floating covers, and variable vapor space tanks.

The second approach to controlling evaporation losses from fixed roof storage tanks includes retrofitable control technology such as internal floating roofs and vapor recovery systems. Internal floating roofs are large pans or decks which float freely on the surface of the stored liquid. The roof rises and falls according to the depth of the stored liquid. To insure that the liquid surface is completely covered, the roof is equipped with a sliding seal around its periphery which fits against the tank wall.

Internal floating roofs reduce evaporative storage losses by minimizing the quantity of exposed liquid surface area available for evaporation. Emissions from internal floating roofs are similar to those from exposed floating roof tanks.

Vapor recovery systems can also be installed on existing fixed cone roof tanks. Vapors generated in the fixed roof tank are displaced through a piping system to a storage tank called a vapor saver. The vapor saver evens out surge flows and saves a reserve of vapors to return to the storage tank during inbreathing modes. Inbreathing saturated hydrocarbon vapors instead of air prevents the evaporation of additional hydrocarbons. Several storage tanks can be manifolded into a single vapor saver and vapor recovery system.

CONTROL METHOD EFFICIENCIES

Incineration of the absorber vent gas can remove more than 95% of combustible materials. Flaring is slightly less efficient, but more than 90% of the combustibles can be removed (5). Ninety to ninety-eight percent control efficiencies can be achieved on storage tanks by substituting lower loss tanks or retrofitting existing tanks with controls (20-22).

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(20) Evaporation Loss from Fixed Roof Tanks. Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

(21) Use of Internal Floating Covers for Fixed Roof Tanks to Reduce Evaporation Loss. Bulletin 2519, American Petroleum Institute, New York, New York, 1962.

(continued)

ECONOMICS

An EPA report addresses the economic impact of installing incinerators on absorber vents of acrylonitrile plants and waste heat boilers on plant incinerators (5). The cost to industry was judged insignificant.

Costs for storage tank controls are available in the literature. Product recovery effectively decreases the cost of these controls.

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(22) Evaporation Loss from Floating Roof Tanks. Bulletin 2517, American Petroleum Institute, New York, New York, 1962. 14 pp.

SECTION 6

REGULATORY ACTION IN PROGRESS

The Occupational Safety and Health Administration (OSHA) has established the threshold limit-value of 45 mg/m^3 as a work place exposure standard. A downward revision of the standard has been promulgated at 4.5 mg/m^3 as an emergency temporary standard (23) and is presently being legally contested by DuPont and other chemical companies. This action follows an announcement by Du Pont that its workers, exposed to acrylonitrile, have experienced high cancer incidence rates (24).

Acrylonitrile use as a grain fumigant is being considered for cancellation under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The substance is also registered under the gasoline additive provisions of the Clean Air Act.

The Food and Drug Administration has regulated the unreacted monomer content of nitrile rubber that comes into contact with food at 11 ppm, and has banned plastic soft drink bottles made of acrylonitrile. Also, acrylonitrile is a priority pollutant for regulation under the Federal Water Pollution Control Act.

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(23) Federal Register, Part IV 43(11):2586, January 17, 1978.

(24) DuPont Reports Problems with Acrylonitrile. Toxic Materials News, 4(17):108, May 25, 1977.

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23. Federal Register, Part IV 43(11):2586, January 17, 1978.

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